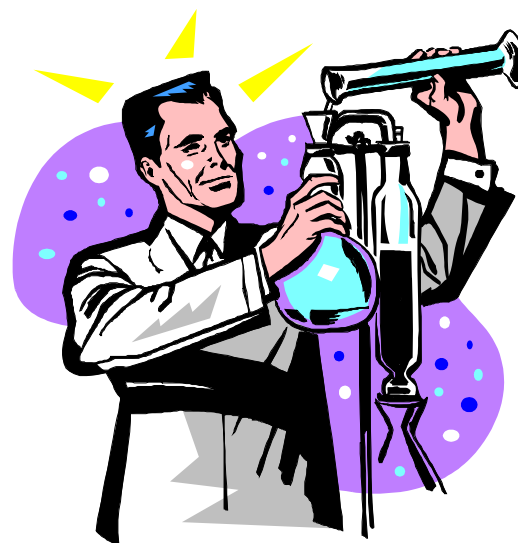


# Nature of Classical Analysis



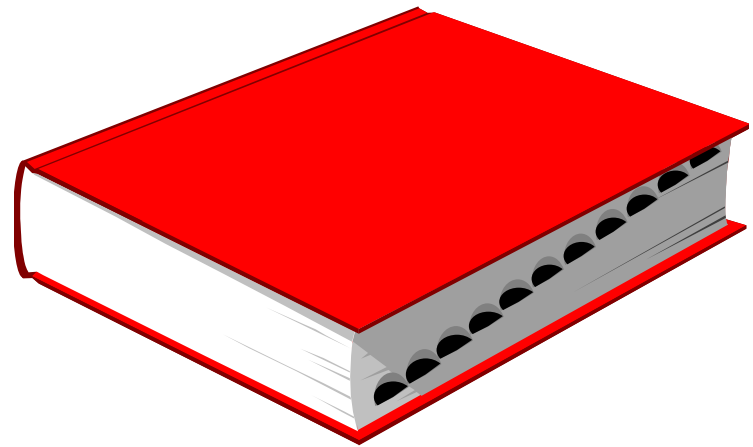
- ★ all sources of error in measurement can be evaluated and expressed in SI units
  - gravimetric analysis
    - » errors due to precipitate purity
  - titrimetric analysis
    - » errors due to selectivity
    - » titrant must be calibrated
      - typically against 1° standard



# For simple dilute solutions...



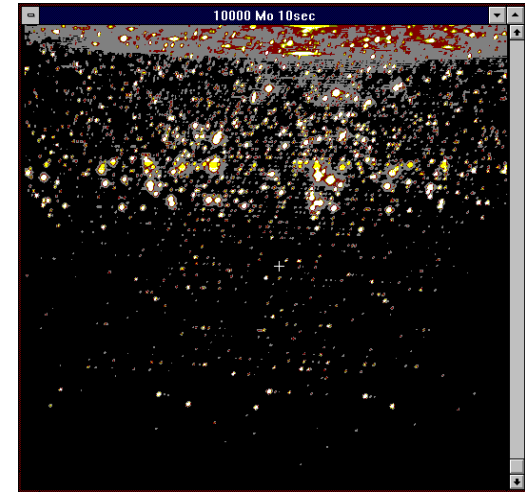
- ★ ICP-OES matches precision of classical analysis
- ★ approaches complete understanding of the sources of error
- ★ potential as “definitive” measurement



# Modern ICP-OES



- ★ integrating solid-state detector
  - high precision photometry
  - simultaneous multi-wavelength
    - » simultaneous background correction
      - no flicker noise penalty for background correction
    - » simultaneous internal standardization
      - high precision ratio measurements
- ★ sample input performance improvements
  - precision, sensitivity, washout, sample tolerance



# ICP-OES equipment used here



- ★ Perkin-Elmer Optima 3000 XL axial ICP-OES

- segmented array detectors

- ★ sample input

- Meinhardt concentric nebulizer
  - » quiet spray
- “Cyclone” spray chamber
  - » fast wash-out, little sample carry-over
  - » “conditioned” with 2% HF to improve wettability

In order to adequately describe experimental procedures, it is occasionally necessary to identify commercial products by manufacturer's name or label. In no instance does such identification imply endorsement by the National Institute of Standards and Technology, nor does it imply that the particular products or equipment are necessarily the best available for that purpose.



# Time Correlated Internal Standard

*Spectrochimica Acta*, Vol. 38B, No. 9, pp. 1227–1253, 1983.  
Printed in Great Britain.

0584-8547/83 \$3.00 + .00  
© 1983. Pergamon Press Ltd.

## Improved performance using internal standardization in inductively-coupled plasma emission spectroscopy

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(Received 30 June 1982, in revised form 25 February 1983)

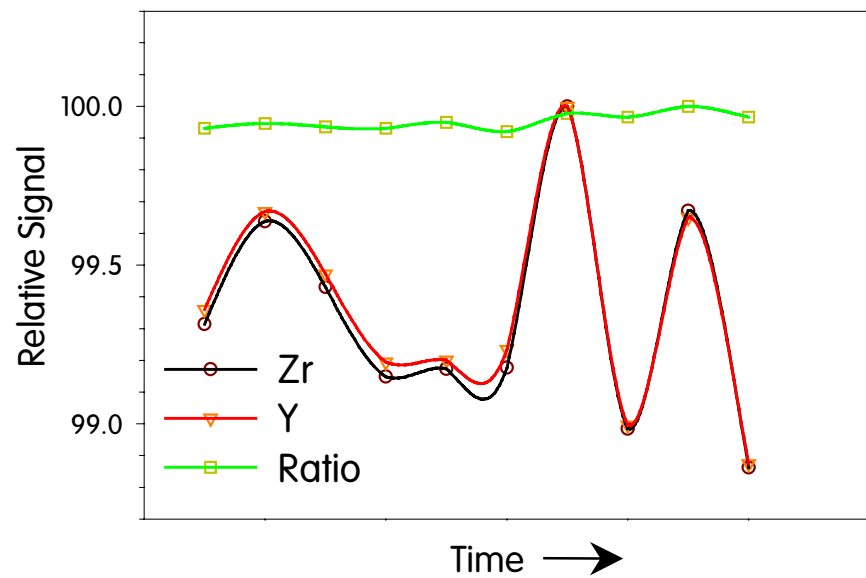
**Abstract**—Significantly improved performance in ICP emission spectroscopy is possible using internal standardization given the proper choice of operating conditions. A dual monochromator detection system was used to study the correlation between two emission signals recorded simultaneously as several ICP parameters were varied. The behavior of the signal formed by dividing the analyte and reference signals was also measured.

The noise behavior of twenty analytically important elements was compared to that of a manganese ion line used as the internal standard for a single, compromise choice of ICP operating parameters (RF power = 1250 W, carrier gas flow rate = 0.7 or 0.9 l/min, and viewing height = 20 mm). The elements differed widely in excitation and ionization energies. Sample concentrations were chosen so that the analyte emission signals were sufficiently intense that the noise and drift contributions due to plasma background and shot noise could be ignored. Under these conditions very good signal correlation ( $r \geq 0.95$ ) and similar noise proportionality factors were observed leading to noise reductions of  $\geq 10 \times$  after signal division in almost every instance. After signal division the noise, defined as the relative standard deviation of the emission signal, (time constant = 1.0 s,  $n = 20$ ) was less than 0.1%. The closely similar noise behavior is attributed to sample density fluctuations arising from corresponding fluctuations of the sample aerosol density. Good correlation is also observed between fluctuations in the plasma background simultaneously detected at two widely separated wavelengths when appropriate steps are taken to reduce shot noise.

At carrier gas flow rates above 1.0 l/min and at viewing heights below 15 mm or above 20 mm, the signal correlation is reduced or absent, yielding little or no improvement using internal standardization.

The use of internal standardization leads to other improvements in analytical performance in addition to noise reduction. Drift is reduced, and nebulizer performance is improved in that it is less sensitive to variations in liquid sample uptake rate, or nebulizer instabilities associated with high solids content sample introduction. The divided signal takes much less time to reach equilibrium following introduction of a new sample.

- ★ precision enhancement
  - matched internal standard
  - can be ~20x improvement



# Internal Standard Selection

“the choice of a good analysis line pair is more complex than implied by the traditional “rules” ...the probability for success has been enhanced as a result of a better understanding of some of the fundamental processes governing intensity ratio behavior in a spectral source.”

Spectrochimica Acta, Vol. 26B, pp. 189 to 191. Pergamon Press 1970. Printed in Northern Ireland

## An experimental study of internal standardization in analytical emission spectroscopy\*

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(Received 10 September 1969)

**Abstract**—Several of the important principles for choosing a good internal standard element and line were examined experimentally, utilizing the induction-coupled plasma as the spectral source. This discharge was chosen because it avoided some of the problems presented by more conventional sources and could be easily profiled spatially to study intensity ratio behavior as temperature, sample density, and electron density varied. In addition, some attention was given to sample distribution in the plasma and its temperature characteristics. Comparisons are presented which demonstrate the relationship between experimental results and those calculated using a computer model developed in an earlier paper.

★ *selection of line pairs is based upon*

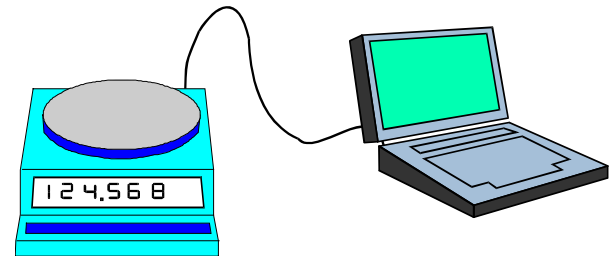
- *excitation energy matching*
- *wavelength matching*
- *periodic adjacency*

# Gravimetric Internal Standardization



- ★ gravimetric preparation

- more accurate
- more easily precise



- ★ experimental procedure

- single batch of diluent with internal standard
- balance 🖐️ computer interface
  - » mass of analyte, mass of diluent w/IS
  - » excellent precision for sample handling

# Internal Standard Calculations



- ★ internal standard is present at different levels in every sample
  - account for variable dilution of internal standard element
- ★ typically perform 2-stage dilution
  - precision better than 1 part-per-thousand

Analyte dilution factor: 
$$D_{\text{analyte}} = \left( \frac{g_{\text{analyte}}}{g_{\text{total}}} \right)$$

Internal Standard dilution factor: 
$$D_{IS} = \left( \frac{g_{\text{total}}}{g_{\text{total}} - g_{\text{analyte}}} \right)$$

Analyte-to-signal ratio relationship: 
$$C_{\text{analyte}} \propto \frac{S_{\text{analyte}}}{S_{IS}} D_{IS}$$

Concentration of analyte in sample: 
$$C_{\text{analyte}}^0 \propto \frac{S_{\text{analyte}}}{S_{IS}} D_{IS} D_{\text{analyte}}$$



# Spectrometric Solution SRMs

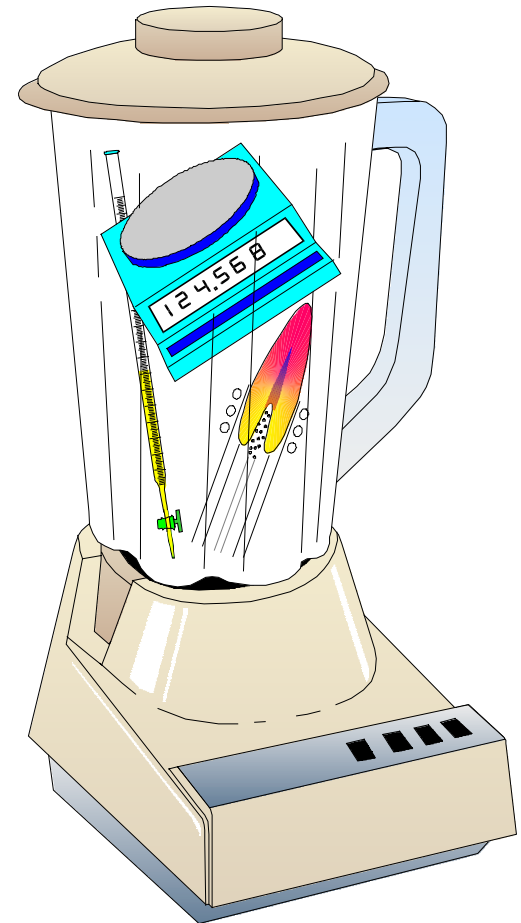


- ★ NIST produces and certifies 63 single element and 3 multi-element Spectrometric Solution SRMs
  - 1000's sold annually for calibration of ICP, AAS
  - typically at 10,000  $\mu\text{g/g}$  levels
  - target uncertainty of  $\sim 0.3\%$  for single element,  $\sim 1\%$  for multielement



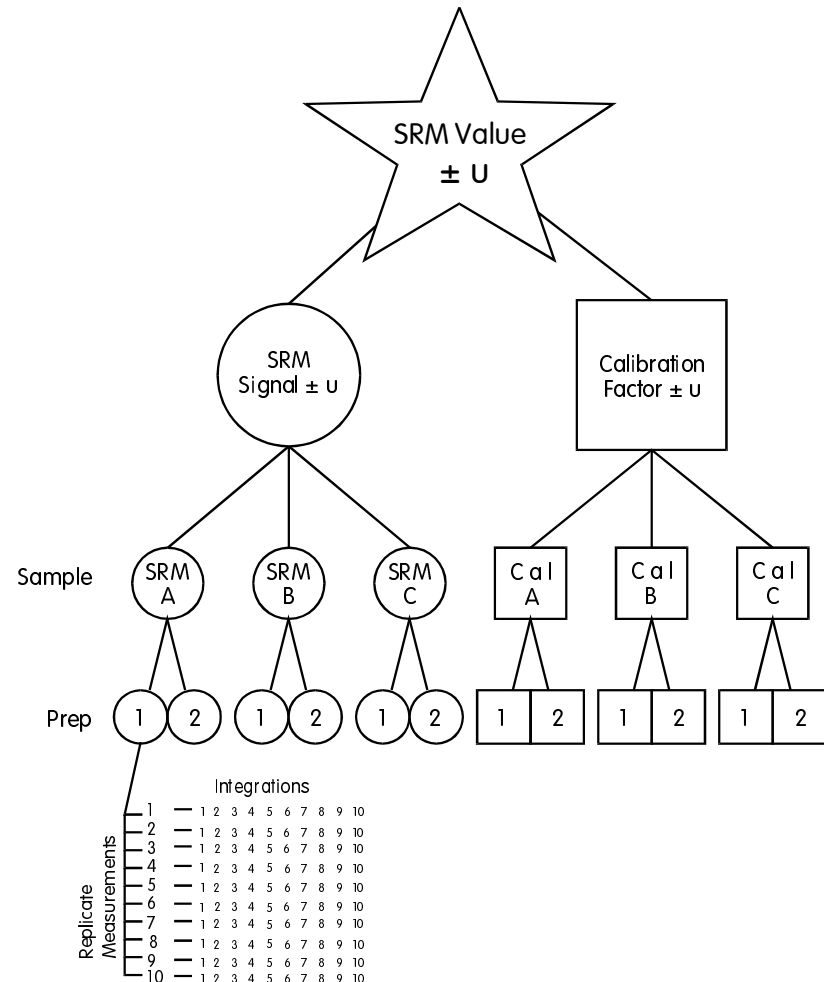
# ICP-OES Role in SRM Program

- ★ analytical measurement combined with gravimetric preparation
  - values and uncertainties blended
- ★ precision comparison against 3 independent calibration standards
  - » different source materials
  - » different preparations in smaller amounts



# Experiment Design

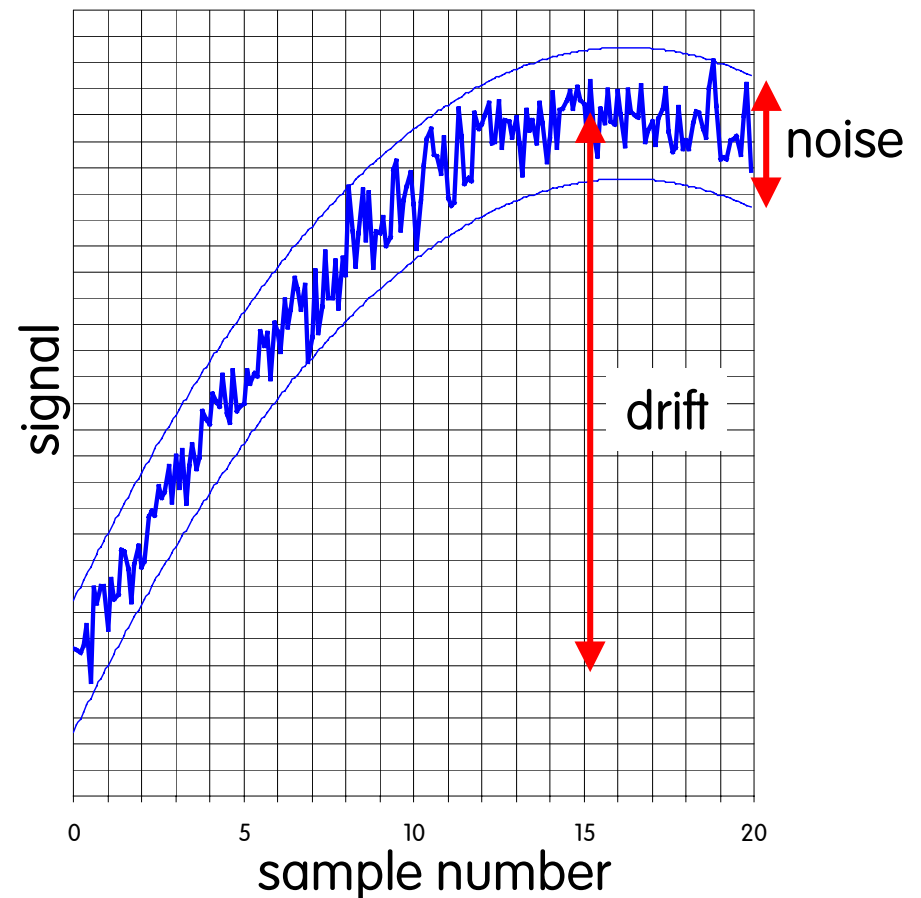
- ★ captures variability due to...
  - standard materials and preparation
  - SRM solution homogeneity
  - solution-to-solution sample preparation
- ★ design for precision measurement
  - long integration times
    - » 10s integration time
  - multiple integrations, measurements
    - » 8-10 replicate integrations
    - » 8-10 replicate measurements



Drift is major  
source of  
uncertainty

# Signal Measurement Errors

- ★ Characterize signal errors as noise or drift
  - “Noise” is short-term imprecision, within measurement of a sample
  - “Drift” is long-term imprecision, occurring over multiple samples



# Drift Correction



$$S_{measured} = S_{truth} + \epsilon_{drift} + \epsilon_{noise}$$

- ★ separate variables to estimate drift as  $f(t)$ 
  - use grand mean for sample to estimate  $S_{truth}$ 
    - » create time series of deviations from mean
      - use *ALL* standards and samples
      - this is our estimate of  $(\epsilon_{drift} + \epsilon_{noise})!$ 
        - use relative deviations for multiplicative drift, absolute deviations for additive drift
  - fit smooth function to these deviations
    - » this is our estimate of  $\epsilon_{drift}!$

# Efficient Drift Correction



- ★ What does an experiment look like?
  - 5 samples, 5 replicate measurements

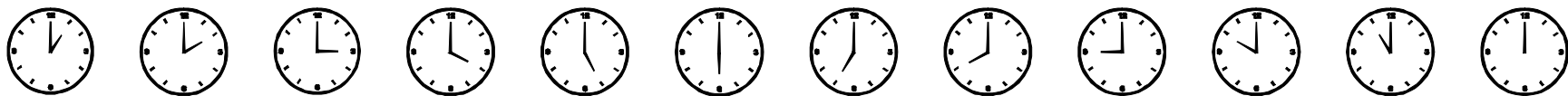
Experiment design for traditional drift correction



Experiment design for efficient drift correction



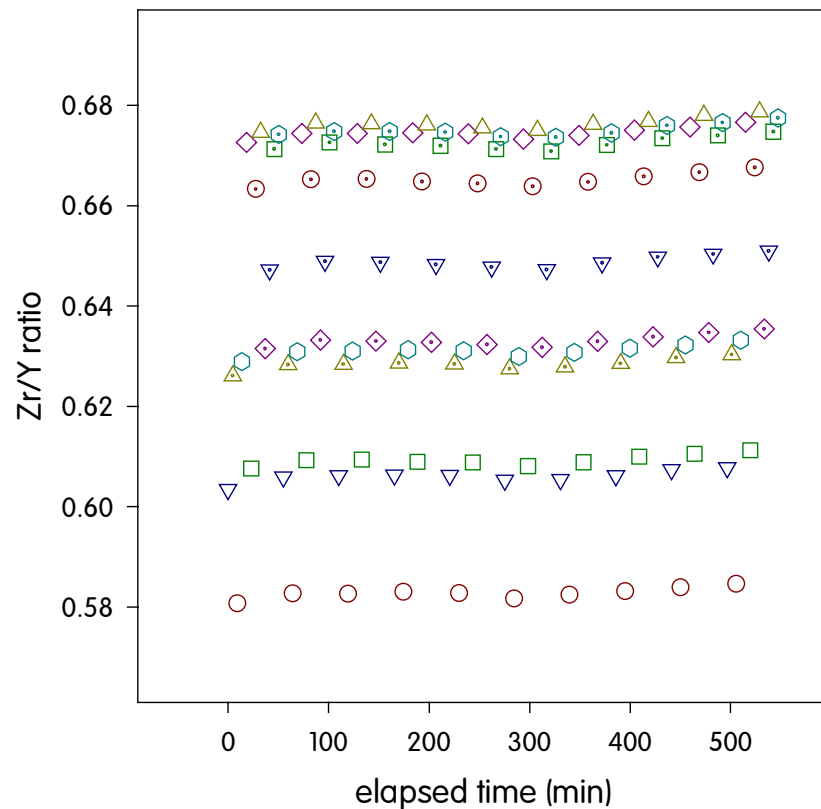
■ Standard  
■ Sample 1  
■ Sample 2  
■ Sample 3  
■ Sample 4  
■ Sample 5



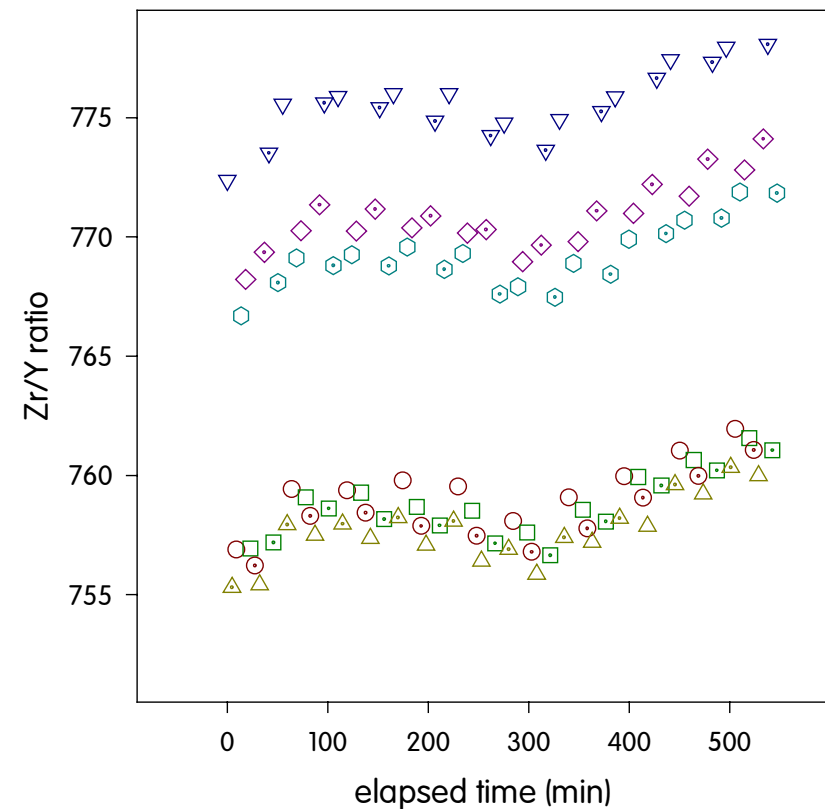
# Zr/Y Results Corrected for Dilution



Data as measured



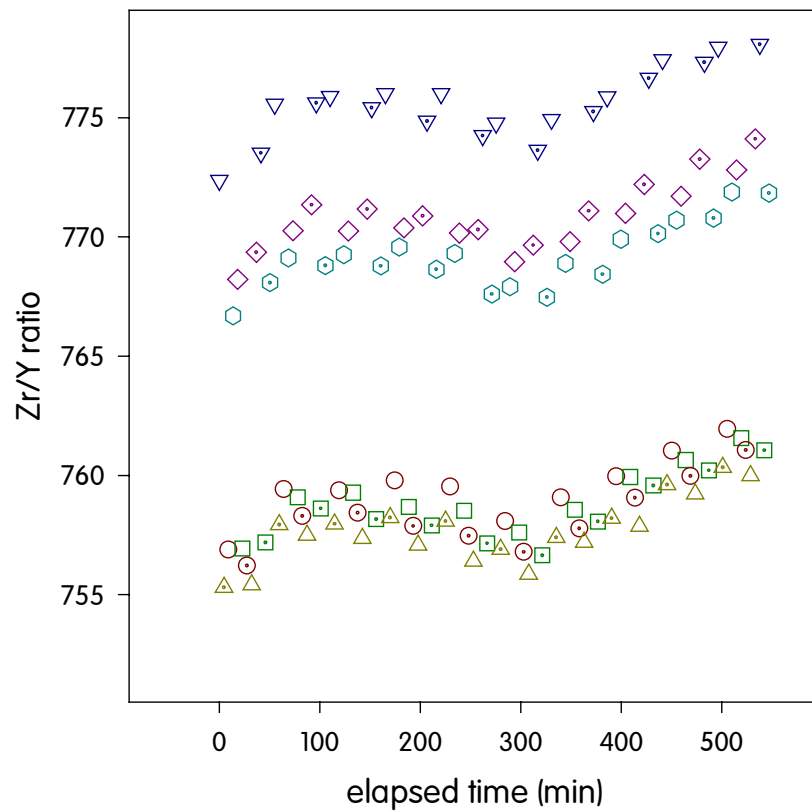
Data after correction for dilution



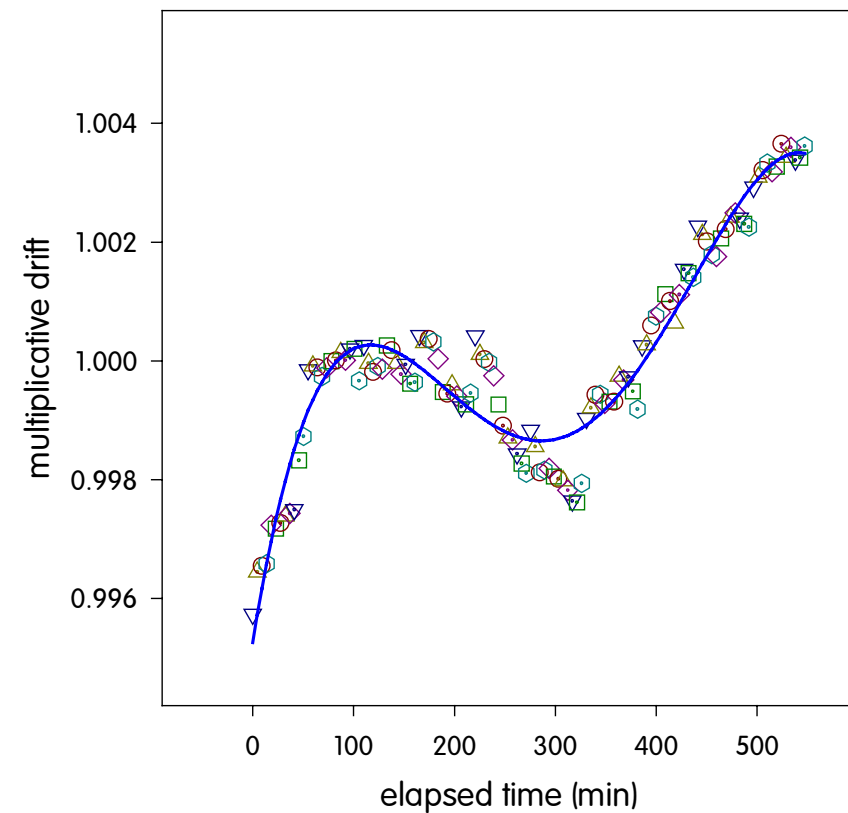
# Drift Model



Data after correction for dilution



Relative Deviations — Drift + Noise

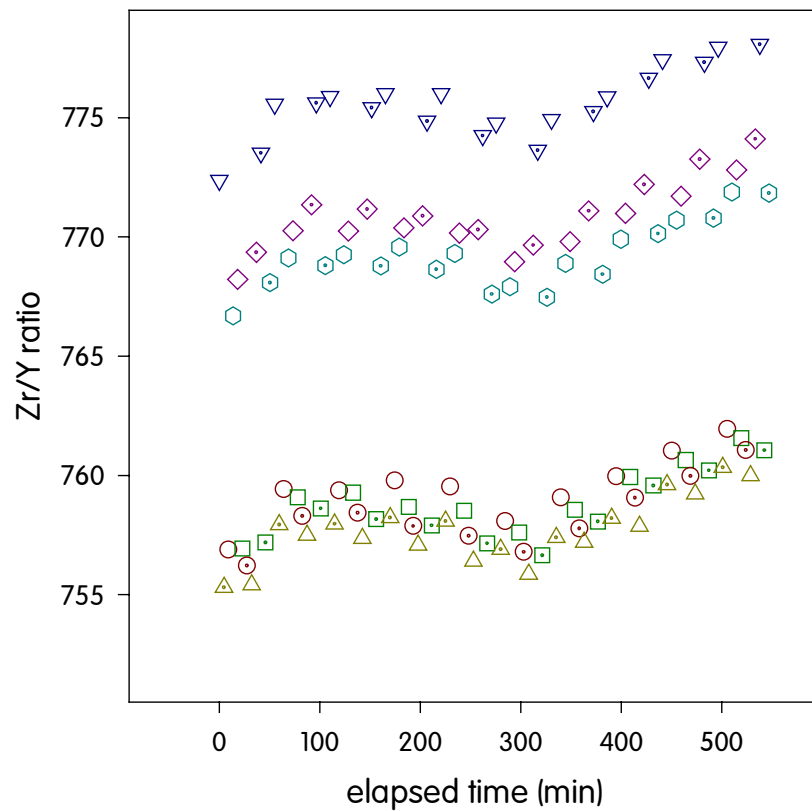




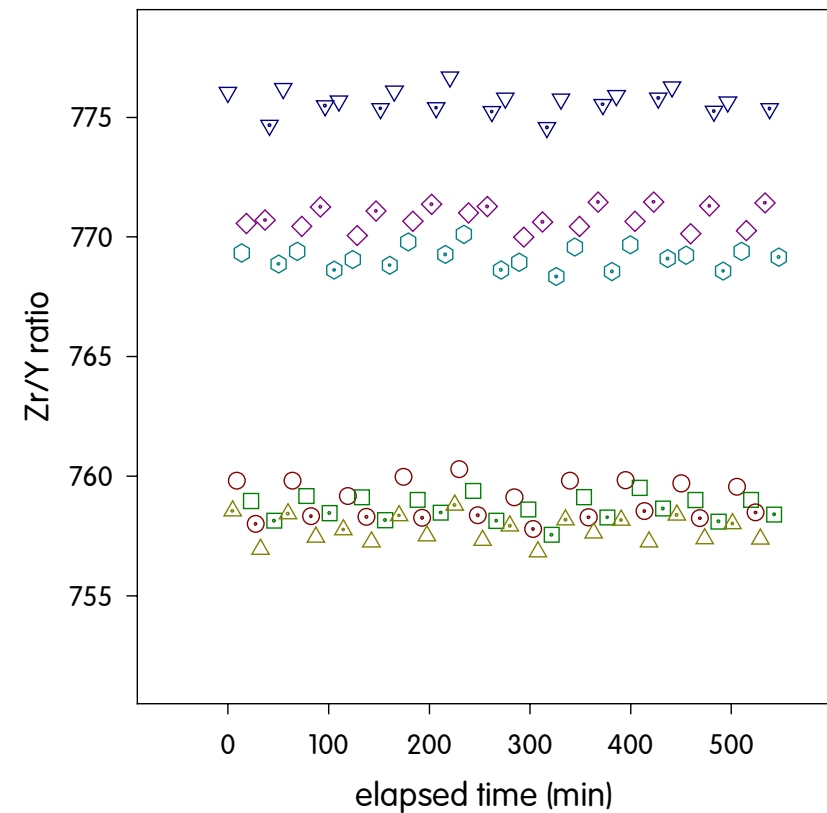
# Drift Corrected Results



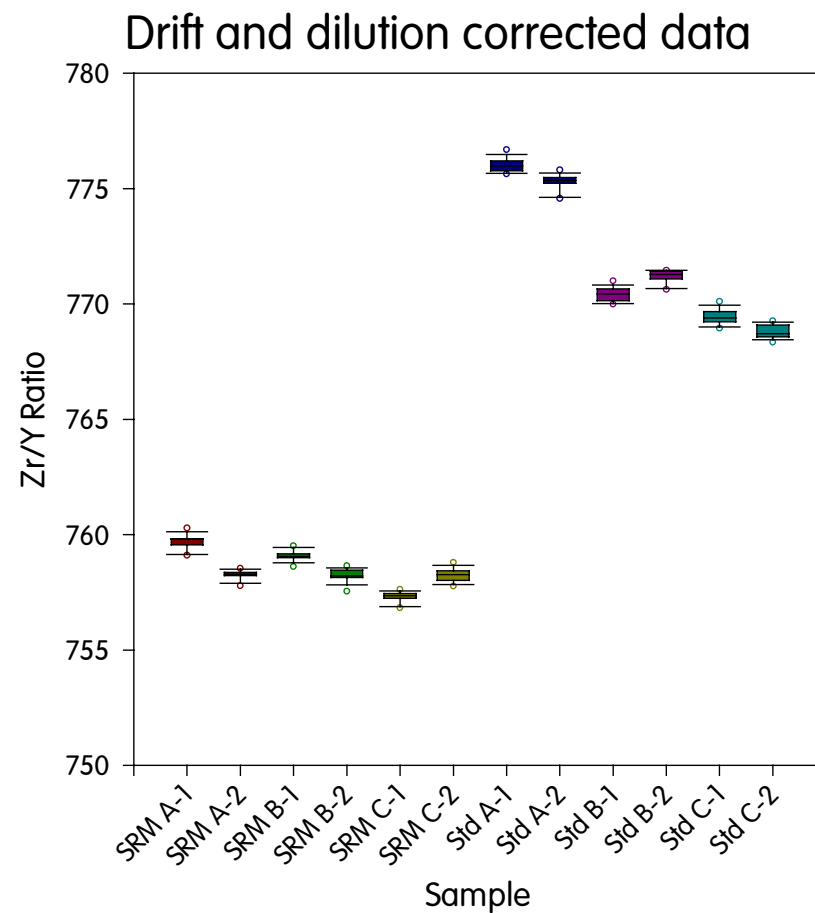
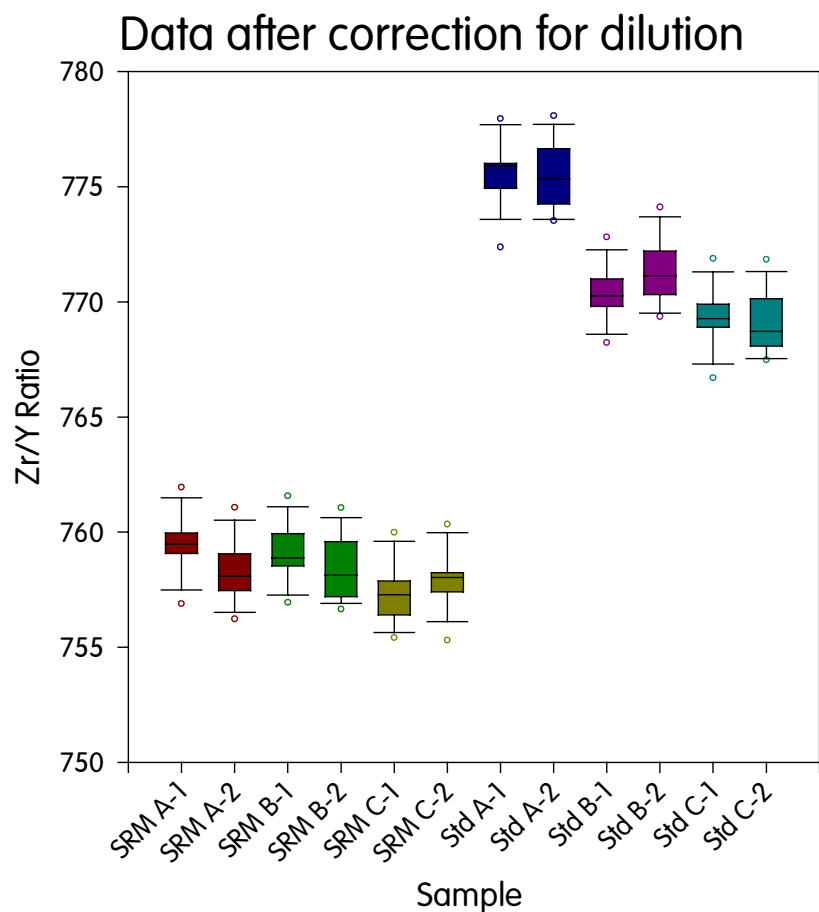
Data after correction for dilution



Drift and dilution corrected data



# Concentration Resolution



# ICP-OES Instrumental Precision



	Analyte	Wavelength (nm)	Internal Standard	Wavelength (nm)	Relative Standard Error for sample
single element	Zr	343.823	Y	360.073	0.019%
	Pt	214.423	Ir	224.268	0.014%
	Sb	206.833	Zn	213.856	0.048%
	As	193.696	Se	196.026	0.094%
	V	292.402	Mn	294.920	0.013%
	Ge	209.426	Zn	213.856	0.040%
	Re	197.240	Ir	224.268	0.073%
	Li	670.781	Rb	780.020	0.056%
	Al	396.152	Mn	403.076	0.017%
multielement	Li	610.364	Mn	403.076	0.047%
	Ba	233.527	Sc	357.253	0.018%
	Ca	317.933	Sc	424.683	0.031%
	Cd	214.438	Sc	357.253	0.042%
	Co	228.616	Sc	357.253	0.019%
	Cr	205.552	Sc	357.253	0.023%
	Cu	324.754	Sc	424.683	0.038%
	La	379.478	Sc	424.683	0.012%
	Li	610.364	Sc	424.683	0.044%
	Mo	202.030	Sc	357.253	0.027%
	Ni	232.003	Sc	357.253	0.011%
	Sr	460.733	Sc	424.683	0.056%

# Components of Uncertainty



- ★ variability of signal measurement
  - samples & calibrants
- ★ variability of solution handling
- ★ uncertainty in calibration material purity
- ★ < 0.1% using new drift correction approach
- ★ ~0.1%
- ★ 0.05% to 0.2%

*ICP-OES performance for analysis of Spectrometric Solution SRMs approaches the level needed to be considered as a definitive method.*